

ROLE OF FUEL REACTIVITY IN SINTERING

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Introduction

The sintering process is used to agglomerate the smaller sizes of iron ores that are too small to be fed directly into the blast furnace. In this process, a heterogeneous mixture of iron ore, fuel, and usually flux is deposited as a bed about 8 to 15 inches deep on an endless, moving sinter strand. The strand moves over a series of windboxes that by means of suction draw a downdraft of air through the bed. As the bed moves into position over the first windbox, the fuel in the top of the bed is ignited by gas burners. After ignition, the air flow through the bed sustains the oxidation reaction and at the same time causes the combustion zone to propagate downward to the bottom of the bed. In this manner, only a comparatively small region (combustion zone) of the bed is being heated to sintering temperatures at any one time. Much of the heat released in the combustion zone is then transferred by forced convection, radiation, and conduction to preheat the portion of the bed lying beneath the advancing combustion zone. Thus, because of good heat recovery, the process requires only a small amount of fuel (about 3 to 5% carbon).

The fuel is randomly distributed throughout the bed and may be considered as discrete particles embedded within a massive matrix of inert material. Furthermore, because of the low concentration of fuel in the bed, the fuel particles are well dispersed and can be visualized as distinct entities oxidizing essentially independently of each other when enough air is available for their combustion.

The combustion process can be considered¹⁾ to occur in two regions, as follows: (1) the region where true chemical reaction controls the oxidation rate, and (2) the region in which the mass transfer of oxygen from the bulk gas stream to the carbon surface is controlling. At temperatures below about 1500 F, the reaction rate is independent of air velocity, whereas above this temperature the rate of combustion is directly influenced by velocity and is limited by the mass transfer rate of oxygen. Kuchta, Kant, and Damon²⁾ have shown that in the second region the reaction rate is proportional to the 0.47 power of the air velocity. Furthermore, at very high air velocities the rate approaches that given by the Arrhenius equation for an activation energy of about 30 k cal/g mole. Meyer³⁾ reported similar activation energies and he as well as Mei Chio Chen, et.al.,⁴⁾ showed that the oxidation of carbon is first order with respect to the partial pressure of oxygen.

Wicke⁵⁾ suggests that for the combustion of carbon the activation energy is about 58 k cal/g mole and that lower values than this are probably due to diffusional effects in the porous interior of the carbon. He further states that differences in reactivity are due solely to variations in internal surface area and that depending upon the type of carbon being oxidized, the specific surface may increase by as much as 1400 percent as carbon is gasified. Smith and Polley⁶⁾ report similar results for the oxidation of fine thermal carbon at 600 C. They concluded that because the increase in surface area is not accompanied by a decrease in particle diameter, the particle must develop internal porosity. These results are in accord with Wicke's and tend to confirm his observation that a reaction also occurs on the internal carbon structure. The bulk of the work reported in the literature for oxidation rates of carbon has dealt with low-ash-content materials. However, Grendon and Wright⁷⁾ have studied the combustion of cokes and coals as well as low-ash carbons

through ash barriers. They advance the possibility that the permeability of the residual ash layer surrounding partially burnt commercial fuels influences the burning rate.

Schluter and Bitsianes⁸⁾ have used the combustion model proposed by Tu et.al¹⁾ in an attempt to predict the width of the fuel combustion zone present in sintering processes. In general, the measured widths were two to three times larger than those predicted. In a prepared discussion of their paper, they have stated that since the rate of combustion of fuel in the sintering process is diffusion controlled, the reactivity of the fuel should have little effect on the processes inherent in sintering. However, no experimental data are presented in substantiation. Furthermore, their model is limited to a case where the fuel is assumed to be a dense sphere of shrinking radius that burns only on its surface and hence cannot allow for the effect of porosity and ash that would affect the diffusional resistances.

Dixon and Voice⁹⁾ state that the sintering process demands a relatively unreactive fuel. Too high a reactivity lowers the thermal efficiency of the process and necessitates a higher fuel content in the sinter bed. For example, with fuel reactivities varying from critical air blast (C.A.B.) values of 0.092 to 0.035 ft³/min, no appreciable effect on the thermal efficiency of the sintering process was noted. However, with a highly reactive wood charcoal (C.A.B. = 0.003 ft³/min), there was a considerable drop in thermal efficiency.

The present paper gives the results of a study completed with eight different fuels for characterizing the fuels with respect to their performance in the sintering process, in which a unique combustion situation exists. The oxidation kinetics of cokes containing different amounts of ash are also included. From these studies, a reactivity index is developed for classifying fuels with regard to their behavior in the sintering operation.

Materials and Experimental Work

The materials used in this work were commercially available cokes, coals, and charcoal. The chemical composition and the physical properties are given in Table I.

A Stanton Thermobalance,^(a) two rotameters, and associated hardware for transporting a synthetic air mixture to the reaction chamber were used in this work. Figure 1 is a schematic drawing of the experimental assembly.

The Thermobalance is an integral unit housing a continuously recording temperature controller, a height-adjustable muffle furnace, and an automatic continuously weighing and recording analytical balance. Mounted on one pan of the balance is a silica rod for supporting a fuel sample in the muffle furnace. The furnace may be raised or lowered by means of pulleys to provide access to the sample holder. Furnace temperatures are indicated and controlled by means of a thermocouple located near the furnace wall (see Figure 1). Two other thermocouples situated directly above and below the carbon sample measure the incoming and exit gas temperatures. For all runs, except for the temperature study, the muffle furnace was set at a control point of 1250 plus or minus 4 F.

A typical run was made as follows: the furnace was set at the desired temperature and allowed to come to equilibrium with a synthetic air mixture flowing through the furnace at a flow rate of 11 liters per minute. The coke sample (0.5000 gram each) obtained by riffing a large batch of coke (-20 +28 Tyler mesh) was dried at 130 C for two hours prior to weighing. The sample was then placed in an inconel wire basket having inside dimensions of 0.6 by 0.6 by 0.5 inch. The bed depth of the coke sample in the basket was 0.12 inch. After the basket containing the coke was placed on the silica support rod of the Thermobalance, the muffle furnace was lowered in place; the loss of weight with time was recorded continuously.

(a) Made in England and distributed by Burrell Scientific Company.

Theory

In the manner proposed by Tu et.al.,¹⁾ it can be shown that the combustion rate of carbon is given by

$$N_c = \frac{p_g}{R_d + R_c} \quad (1)$$

where p_g is the partial pressure of oxygen in the bulk gas stream (atm)
 R_d is the diffusional resistance to mass transfer (hr)(atm)/lb mole
 R_c is the chemical resistance (hr)(atm)/(lb mole)
 N_c equals the rate of carbon consumption (lb moles/hr)

Now if reaction conditions are chosen such that chemical reaction controls the rate of carbon consumption, that is, $R_c \gg R_d$, equation (1) reduces to

$$N_c = \frac{p_g}{R_c} = ak p_g \quad (2)$$

where a = area available for reaction
 k = the specific reaction rate constant as given by the Arrhenius equation

In the case of a packed bed of particles having appreciable depth, p_g varies with the depth of the bed. Hence, under isothermal conditions, it becomes necessary to integrate equation (2) between the limits of the inlet and outlet gas compositions to obtain the average value of the rates existing in every part of the bed. Generally it is difficult to maintain isothermal conditions, because the oxidation of carbon is highly exothermic and the reaction temperature tends to rise. However, by use of a differential reactor, rising temperatures are easily treated because rate data may be obtained at each incremental temperature change. Under these circumstances, equation (2) becomes

$$N_c = \alpha a \quad (3)$$

where α is a constant

Equation (3) describes the oxidation of carbon in a chemical-reaction-controlled regime. However, the sintering process occurs at high temperatures of about 2700 F. In this region, the oxidation rate of carbon is controlled by the mass transport of oxygen from the bulk gas phase to the carbon surface; that is, diffusional resistance is much larger than the resistance due to chemical reaction. Hence the carbon combustion can be approximated by modifying equation (1) to

$$N_c = \frac{p_g}{R_d} = k_g a p_g = \frac{DPa}{RTz p_{bm}} p_g \quad (4)$$

where D = diffusion coefficient (ft²/hr)
 R = gas constant (ft³)(atm)/(lb mole)(°R)
 P = total pressure (atm)
 k_g = mass transfer coefficient (lb moles)/(hr)(ft²)(atm)
 z = effective film thickness (ft)
 T = temperature (°R)
 p_{bm} = log mean pressure of inert gas in the film

Equation (4) implies that in a diffusion-controlled regime, the oxidation rate is independent of the carbon being burned and depends only on the transport of oxygen. Within limits, this is true; but with cokes or carbons of widely different porosities and varying ash contents, the effective film thickness (z) and the area available for reaction (a) may be vastly different at identical air flow rates. Second, with fuels having a high ash content, it is known that an ash structure can surround the unburnt carbon⁷⁾ and may impede combustion through its effect on the diffusion

coefficient. Thus the properties of the fuel can influence the combustion rate of carbon in the sintering-temperature (diffusion-controlled) region.

Results and Discussion

The Effect of Temperature on the Oxidation Rate of Coke

Most of the kinetics work was performed with coke C because it had been found to be an excellent fuel for sintering. In the study of the effect of temperature on the oxidation rate, the correlating temperatures were the exit gas temperatures leaving the bottom of the differential reactor. In general, these temperatures are about 150 F higher than the furnace temperature. But optical-pyrometer measurements of the top of the packed bed of particles at temperatures above 1400 F gave temperatures about 25 to 50 degrees higher than the exit gas temperatures. Visual observation of the bed showed a considerable nonuniformity in burning; discrete particles of coke could be seen burning more brilliantly than others in various parts of the bed. Consequently, exit gas temperatures were assumed to be representative of the bed temperature.

The results of the oxidation tests at various temperatures are presented in Figure 2. In these tests, the exit gas temperature increases and reaches a maximum and thereafter decreases with time to a constant level. For proper evaluation of the reaction rate, the weight-loss data must be corrected for volatile matter. This was done by heating the coke to various temperatures in N_2 and obtaining devolatilization rate curves. The volatile matter loss is then subtracted from the gross weight loss to obtain the weight loss due to oxidation.

With these data, an Arrhenius plot was made of the reaction rate expressed in pound moles of carbon consumed per hour per square foot of total surface area. The results are presented in Figure 3. Also included in this plot are the data given by Wicke²⁾ for electrode carbon. Only at temperatures below about 1400 F do the experimental data lie along the curve given by Wicke. This corresponds to an activation energy of 58 k cal/g mole, which indicates that the oxidation of carbon is controlled by chemical reaction. As the temperature is increased above 1400 F, the effect of diffusion becomes increasingly significant and the data deviate considerably from the straight-line Arrhenius relationship.

From the kinetic data of curve 2, Figure 2, the total surface area of coke C was calculated with the use of a known specific reaction rate constant for electrode carbon. The calculated surface area based on points taken over the entire curve was $3.0 \text{ m}^2/\text{gram}$ (standard deviation 0.39). Experimental nitrogen adsorption (BET) surface-area measurements showed that the surface area of coke C was essentially constant at $3.4 \text{ m}^2/\text{gram}$ at various degrees of oxidation. A similar calculation for charcoal H (Figure 4) at 30 percent weight loss gave a total surface area of $4.8 \text{ m}^2/\text{gram}$, whereas the BET method gave a value of $5.2 \text{ m}^2/\text{gram}$ for a fresh sample. These values indicate that the combustion of different fuels is primarily dependent on the surface area of the material. It should be mentioned that these calculations are based only on the fixed carbon available in the coke sample, whereas the BET method makes no distinction between ash and carbon contributions to the total area. Consequently, for high-ash materials it is expected that the adsorption technique will yield surface areas considerably different from those calculated from the oxidation curves.

These two fuel samples cover the extreme oxidation rates encountered in this report; that is, coke C burns at the slowest rate and charcoal H at the most rapid. As the oxidation rates for both fuels correlate rather well with their BET surface areas, it appears that the gross oxidation phenomenon in a chemical-reaction-controlled regime where excess oxygen is always available is directly related to the total surface area of the solids. However, a more fundamental study would probably reveal that

additional carbon properties such as anisotropy and lattice defects influence the true kinetics of oxidation. In addition, the impurities also have an effect on the oxidation rate.

The Air Oxidation of Various Sinter Fuels

To determine their relative ease of oxidation, eight different fuels were oxidized in air at a furnace temperature of 1250 F. (The compositions of the fuels are given in Table I.) The results of this study are presented in Figure 4.

Each fuel was tested in duplicate runs to check on data reproducibility. Figure 4 indicates that the fuels can be ranked in order of increasing reactivity, that is, ease of oxidation, as follows: C, E, G, F, D, A, and H. Coke B behaves somewhat anomalously in that it has the fastest initial burning rate, but quickly slows down. We believe that because of its high ash content (Table I), the ash can decrease the carbon surface available for reaction and also increase the diffusional path across which the mass transfer of O_2 occurs. Consequently, as more and more carbon is consumed, the ash becomes increasingly significant in preventing the exposure of carbon surface to the oxidizing gas, and the rate of oxidation diminishes.

Several tests were also completed to obtain oxidation data at a furnace temperature of 1600 F. The results of this work are presented in Figure 5. A comparison of Figures 4 and 5 shows that in general the oxidation curves for both low- and high-temperature tests are ranked in the same manner; that is, coke C is still represented as the slowest burning coke regardless of the temperature of oxidation, and similarly for the other cokes. A slight anomaly does exist: the low-temperature work indicates that charcoal D and coke A should behave similarly, whereas the high-temperature data suggest a higher reactivity for the activated charcoal. It is believed, however, that this difference is due to the experimental technique and may be explained as follows. The size of the sample and the cross-sectional area of the reactor basket used in both cases were the same. Consequently, the height of the sample in the basket for coke A as compared with the height for charcoal D varies with the ratio of the apparent specific gravities. Thus the sample height for coke A is 1.48 times that for charcoal D. This has two adverse effects on the oxidation rate: (1) the pressure drop across the basket increases causing more air to flow around the basket rather than through it, and (2) the partial pressure of CO_2 increases in the bed. These two factors tend to depress the reaction rate. At low temperatures, this result is not evidenced because the reaction rate is slow and the air flow is large enough to offset any effects due to changes in partial pressure of oxygen.

A short study was made to determine the variation of the coke particle size with increasing degree of oxidation. These data, for coke C initially minus 20 plus 28 mesh, are presented in Table II. The particle size is relatively independent of the percent oxidation. Even after 87 percent weight loss, the oxidized sample still contained 71.5 percent of the original screen size. This is in agreement with the results reported by others.^{5,6} A sample oxidized at a furnace temperature of 1600 F exhibited considerable fusion of the particles as reflected by the creation of 21.2 percent of a plus 20-mesh fraction. As the initial particle size was all minus 20 plus 28 mesh, the data suggest that at higher temperatures, the oxidation rate of high-ash fuels may be affected by partial fusion or sintering of the ash. In particular, if the ash becomes sufficiently fluid to occlude the surface of the carbon, a corresponding decrease in rate should occur.

The Reactivity Index as a Measure of Fuel Performance in Sintering

In the sintering process, only the fixed carbon is considered to be useful for generating the required heat flux. Voice and Dixon⁹) in summarizing the available literature on the subject report that any heat generated by the combustion of volatiles lowers the thermal efficiency of the sintering process.

As no one property of the fuel, such as ignition temperature, fixed carbon content, or ash content, can adequately describe its behavior during the combustion process, a reactivity index based on 50 percent weight loss of fuel has been defined. For this purpose, we choose to set the air oxidation test conditions just outside of the region in which chemical reaction alone controls the oxidation rate, where the differences in the reactivities of fuels could be easily distinguished. For our equipment, this corresponds to an air flow rate of 11 liters per minute and a furnace temperature setting of 1250 F.

A measure of the reactivity of fuels under these conditions is the area under the percent weight loss versus time curve (Figure 4). In this manner, fuels having a fixed carbon content of as low as 50 percent may be included in this index. The area under the curve is then normalized to place all measurements on a per gram of fixed carbon basis. Thus the reactivity index ϕ is defined as

$$\phi = \frac{\int_0^{t_{50}} \frac{m(t) dt}{m_0/f}}{10^{-4} F} \int_0^{t_{50}} w(t) dt \quad (5)$$

where t_{50} = time for 50 percent weight loss
 $m(t)$ = weight loss in grams as a function of time
 m_0 = initial sample weight (grams)
 f = weight fraction of fixed carbon in sample
 $w(t)$ = percent weight loss of sample as a function of time
 F = percent weight fraction of fixed carbon in sample

The reactivity index ϕ is correlated with sinter production rate as shown in Table III. Sufficient samples were not available for sinter pot tests to be run on all the fuels studied. However, the data establish the general trend. Fuels having a reactivity index greater than 1.65 appear to yield a sinter production rate of about 4.2 tons per day per square foot. These fuels are acceptable for the sintering process. Below an index of 1.65, the production rate decreases. The performance of those fuels having a reactivity index between about 1.35 and 1.65 can be improved by blending with a better-quality fuel. Fuels having an index of less than 1.35 are unsatisfactory for use as sinter fuel.

Fuel Reactivity and the Mechanism of Sintering

We have observed that the oxidation of the more reactive fuels results in a higher carbon monoxide concentration in the waste gas. This is due to incomplete combustion of the fuel and/or the gasification of carbon. In either case, the thermal efficiency of the sintering process is lowered and a higher fuel content in the sinter bed is often required to accomplish the desired result. Highly reactive fuels also tend to minimize thermal efficiency because of their susceptibility to rapid weight loss at relatively low temperatures. The decrease in thermal efficiency may be visualized by considering the temperature profile that exists in a sinter bed.

In general, there are three regions of major interest: the sinter-mix preheat zone, the combustion zone, and the sinter cooling zone.¹⁰⁾ In a downdraft sintering process, these zones leave the bottom of the packed bed in the given order. Consider now only the preheat and combustion zones. As sinter feed mixture passes under the ignition burner, the fuel in the top part of the bed is ignited to initiate the formation of the combustion zone. At the same time, the downdraft of air drawn through the bed is rapidly transferring heat from the combustion zone to the immediately preceding preheat zone. At this particular time, the unreacted fuel in the preheat zone is exposed to temperatures varying between the ambient bed temperatures and those of the approaching flame front. If the fuel is highly reactive, then a significant portion of the carbon may be lost through oxidation with air in the preheat zone. This results in smaller amounts of carbon being available for combustion in the combustion zone, and thus reduces the heat flux for sintering. Furthermore, the

reactive fuel burns quickly and generates an intense heat in a narrow combustion zone. Consequently, the normal heat-transfer process from gas to solid cannot keep up with the rapidly moving combustion zone, and the result is the formation of a weak sinter.

If a less reactive fuel is used, premature oxidation of the carbon in the preheat zone is minimized, and more complete burning occurs. This causes a relative increase in the width of the combustion zone that (1) permits the heat-transfer processes occurring in the bed to operate in phase with the combustion process, and (2) prevents localized melting because more uniform temperatures are obtained in the combustion zone. It is known that excessive fusion tends to cause the sinter bed to slag over and thus to depress production rates, whereas too little fusion results in weak sinter. Consequently, a good sinter fuel will permit operation between these two extremes.

On the basis of the reactivity index, as well as the oxidation data of Figure 4, the results tend to indicate that the slower burning fuels are most desirable for sintering purposes. This is consistent with our present understanding of the sintering process. In general, the reactivity index appears to yield useful information on the expected production rate that may be obtained with a given fuel. It ranks sinter fuels on a relative scale with respect to their performance in the sintering process. The test is particularly useful for the evaluation of small samples.

Conclusions

Evidence is presented that tends to show that in a chemical-reaction-controlled regime, the oxidation kinetics of carbonaceous fuels depend upon the total (BET) surface area of the fuel particles. This is in agreement with the observations of Wicke.⁵⁾

A reactivity test based on the oxidation characteristics of various sinter fuels has been developed. This index correlates with the production rates of iron-ore sinters. In general, the best sinter production rates are obtained when the sinter fuels are slow burning; that is, when they are relatively unreactive.

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TABLE I
The Chemical Composition of Various Sinter Fuels

Fuel	A (coke)	B (coke)	C (coke)	D (charcoal)	E (coal)	F (coke)	G (coke)	H (charcoal)
Sulfur*	0.65	0.78	1.22	0.10	0.57	0.93	3.61	0.11
Fixed Carbon	86.08	60.61	85.40	86.69	74.16	87.75	86.80	86.83
Volatile Matter	6.29	12.87	4.30	5.83	7.80	4.21	12.65	8.16
Ash	4.94	25.51	10.01	4.08	16.26	7.28	0.51	4.55
Total Carbon	86.92	66.32	87.90	88.67	76.47	88.43	90.70	87.80
Moisture	2.69	1.01	0.29	3.40	1.78	0.76	0.04	0.46
True Specific Gravity	1.65	1.69	1.89	1.77	1.70	1.81	----	----
Apparent Specific Gravity	1.05	1.60	1.70	1.55	1.64	1.46	1.33	1.291

*Compositions in weight percent.

TABLE II

The Effect of Air Oxidation on the Particle Size
of Coke C

Percent Oxidized*	0	10	21	40***	67.5	87****
Screen Analysis of**						
Oxidized Fuels (Cumulative %)						
Tyler Mesh						
+20	0	5.1	2.4	-	5.7	21.2
-20 +28	100	96.0	93.1	85.4	77.5	71.5
+35	-	98.6	96.5	91.5	96.0	89.1
+48	-	98.8	96.9	93.2	97.9	92.5
+65	-	98.9	97.3	96.1	99.1	95.4
+100	-	99.0	98.0	97.7	99.6	96.8

* Samples oxidized at a furnace temperature of 1250 F at an air flow rate of 11 liters per minute.

** Screen analysis obtained by hand screening of samples for two minutes.

*** Ro-tapped for 15 minutes.

**** Furnace temperature 1600 F.

TABLE III

The Correlation of Sinter Production Rate With the
Reactivity Index of Sinter Fuels

Fuel	Reactivity Index (ϕ)	Sinter Production Rate Tons/day/ft ²
C (coke)	2.50	4.2
E (coal)	1.84	4.2
F (coke)	1.70	---*
G (coke)	1.68	4.2
D (charcoal)	1.43	---*
A (coke)	1.40	3.8
H (charcoal)	1.25	---*
B (coke)	1.24	3.4

*Insufficient sample to run sinter pot test.

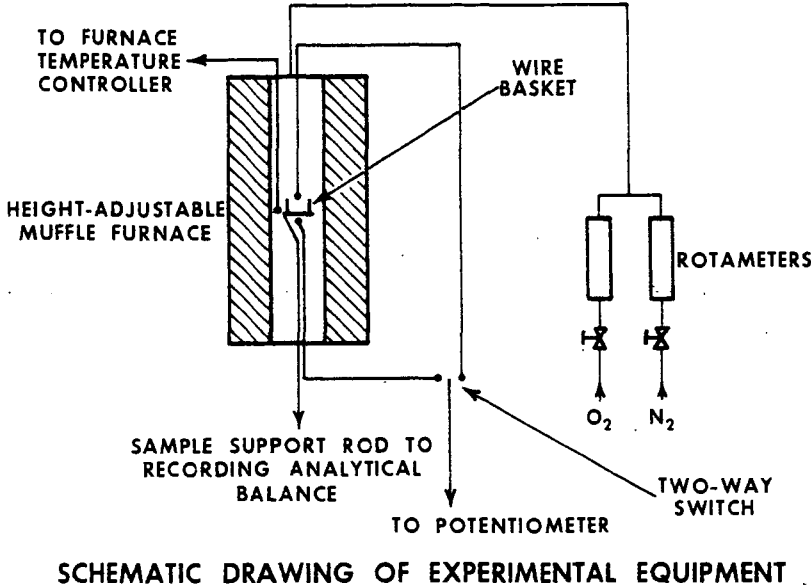


FIGURE 1

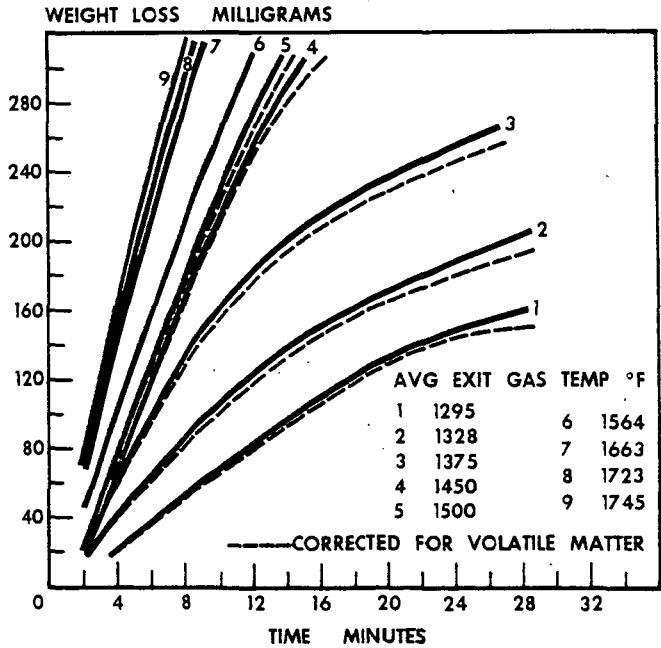


FIGURE 2

AIR OXIDATION OF COKE C AT VARIOUS TEMPERATURES

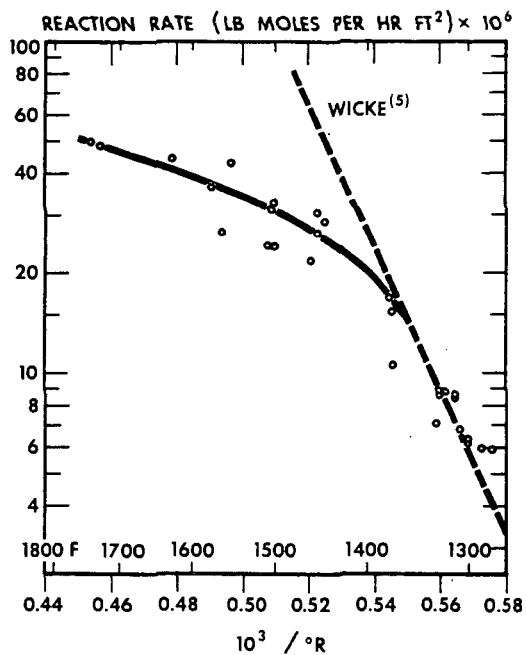


FIGURE 3

EFFECT OF TEMPERATURE ON THE SPECIFIC REACTION RATE OF COKE C

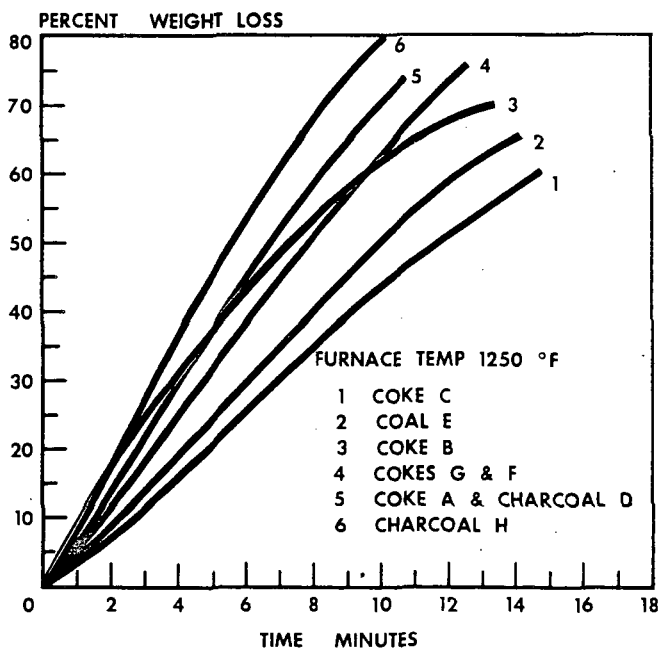


FIGURE 4

AIR OXIDATION OF VARIOUS FUELS

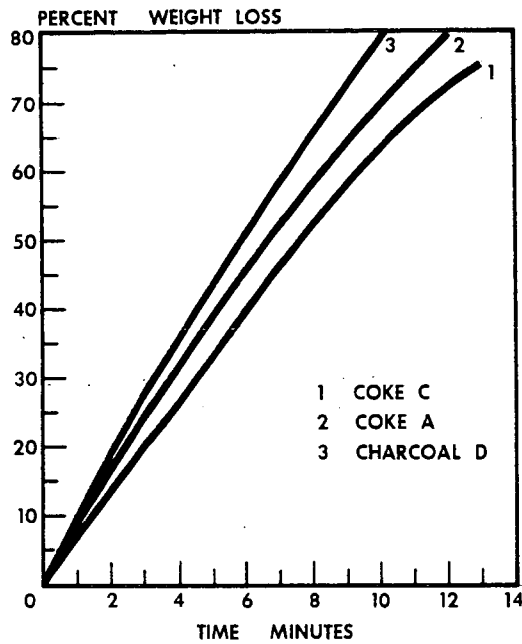


FIGURE 5
AIR OXIDATION OF VARIOUS FUELS AT 1600 F